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(54) Title: BREATHABLE FILM

(57) Abstract: There is provided the use of a ground particulate calcium carbonate material having a  $d_{50}$  of less than  $1.0 \mu$  as a mineral filler in a stretched thermoplastic polyolefin film, for the purpose of increasing the moisture vapour permeability of said film. Also disclosed is a method of increasing the moisture vapour permeability of a stretched, mineral-filled thermoplastic polyolefin film which method comprises using, as the mineral filler, a ground calcium carbonate having a  $d_{50}$  of less than  $1.0 \mu$ .

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BREATHABLE FILMDESCRIPTION OF THE INVENTIONField of the invention

5       The present invention relates to a breathable film, and its uses and preparation thereof.

Background of the Invention

10       Alkaline earth metal carbonates, particularly calcium carbonates are used as the particulate filler in end products comprising compositions incorporating thermoplastic polymers, such as breathable film products. Such films are manufactured for a number of consumer products such as backing materials, plastic  
15       paper, house wrap, roofing membranes, grocery sacks, diapers, bandages, training pants, sanitary napkins, surgical drapes, and surgical gowns. The compositions from which these films are made may include two basic components, the first being a thermoplastic polymer,  
20       usually a predominantly linear polyolefin polymer such as a linear low density polyethylene and the second being an inorganic particulate filler such as calcium carbonate. A third component, namely a bonding or tackifying agent may often be present. These components  
25       are mixed and compounded together to form a compound or concentrate which is formed (usually in a subsequent process) into a film layer using any one of a variety of film-producing processes known to those of ordinary skill in the film making art including casting or  
30       blowing. Alternatively, the film may be laid down on a

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substrate such as paper or board in a process known as extrusion coating.

After the film is fabricated into its desired form, to make a porous breathable film, the film is then stretched, uniaxially or biaxially, by any of the well-known techniques in the art including by hydraulics, by pinch rolls moving at different rates, by interdigitating rolls or by tentering.

Nago et al ((1992); Journal of Applied Polymer Science, Vol. 45, 1527-1535 discloses the preparation of microporous polypropylene sheets by biaxially stretching polypropylene sheets containing a calcium carbonate filler content of 59 % by weight, the calcium carbonate having a particle size of 0.08 - 3.0 %.

#### Summary of the Invention

According to one aspect of the present invention, there is provided the use of a ground particulate calcium carbonate material having a  $d_{50}$  of less than 1.0  $\mu\text{m}$  as a mineral filler in a stretched thermoplastic polyolefin film, for the purpose of increasing the moisture vapour permeability of said film.

According to another aspect of the present invention, there is provided a method of increasing the moisture vapour permeability of a stretched, mineral-filled thermoplastic polyolefin film which method comprises using, as the mineral filler, a ground calcium carbonate having a  $d_{50}$  of less than 1.0  $\mu\text{m}$ .

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DESCRIPTION OF THE INVENTION

The purpose of the present invention is to increase the moisture vapour permeability (or "breathability") of stretched, mineral-filled polyolefin films. This is  
5 achieved in accordance with the invention by using, as the mineral filler, a ground calcium carbonate filler, having a  $d_{50}$  of less than 1.0  $\mu\text{m}$ . It has been found that, when such a ground calcium carbonate is used, the breathability of the stretched polyolefin film is  
10 increased compared with conventional mineral filled polyolefin films in which the mineral filler has a  $d_{50}$  which is greater than 1.0  $\mu\text{m}$ .

The " $d_{50}$ " of the mineral filler used herein is defined as the particle size value less than about which  
15 there are 50% by weight of the particles.

For the purposes of the present invention, a film is "breathable" if it has a moisture vapour transmission rate (MVTR) of at least 100  $\text{g/m}^2/24$  hours as calculated using the test method described in US Patent No.  
20 5,695,868.

In this specification, "film" means a sheet or layer of material having a median thickness of no more than about 250  $\mu\text{m}$ . Typical thickness sizes and properties of films are described later. The film of  
25 the present invention is a breathable film, i.e. having microscopic interconnecting pores not greater than about 30  $\mu\text{m}$  in size (usually much less). Such a film allows for example water vapor in the atmosphere on one side of the film to permeate to the atmosphere on the other side  
30 without liquid water being transmitted through the film.

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The calcium carbonate used in the present invention may comprise a carbonate obtained from a mineral source and processed by refining and treatment processes including grinding to obtain a suitable particle size distribution. The grinding process may be carried out either in a dry state, typically in the absence of added hygroscopic or hydrophilic chemicals or in a wet state in an aqueous medium in which any dispersant employed is minimized and/or subsequently removed from the filler in a known manner. Wet ground material is subsequently dried to an extent such that the particulate material has an appropriate moisture content. The particles of the particulate product according to the present invention are treated (coated) with one of the aliphatic carboxylic acid hydrophobizing surface treatment agents conventionally employed to coat carbonates.

The calcium carbonate used in the present invention may be obtained from a natural source, e.g. marble, chalk or limestone. Desirably, at least 95%, preferably at least 99%, by weight of the calcium carbonate filler comprises the carbonate itself although minor additions of other mineral additives, e.g. one or more of kaolin, calcined kaolin, wollastonite, bauxite, talc or mica, could also be present together with the carbonate. At least 95% to 99% by weight may be calcium carbonate which may be obtained in a well known way by processing naturally occurring calcium carbonate obtained from a mineral source.

The particulate product according to the present invention preferably has one or more of the following particle size properties:

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i. a top cut (the particle size value less than about which at least 99% by weight of the particles of the material have a size) of less than about 10 $\mu$ m, desirably less than about 8 $\mu$ m;

5 ii. a moisture pick up of less than about 0.35% by weight, more preferably less than about 0.2 % by weight, and most preferably less than about 0.1% by weight;

All particle size values as specified herein are measured by the well known conventional method employed  
10 in the art of sedimentation of the particles in a fully dispersed state in an aqueous medium using a SEDIGRAPH 5100 machine as supplied by Micromeritics Corporation, USA.

The ground calcium carbonate filler used in the  
15 present invention may have a  $d_{50}$  of at least 0.3  $\mu$ m, and for example may have a  $d_{50}$  which is greater than 0.5  $\mu$ m. Further, the calcium carbonate may have  $d_{50}$  which is less than 0.8  $\mu$ m.

The calcium carbonate used in the present invention  
20 preferably has a total surface moisture content which is preferably less than about 0.1% by weight even after exposure for 40 hours at 20°C to a moist atmosphere having a relative humidity of 80%. Desirably, the surface moisture content is less than about 0.1% by  
25 weight even after exposure for 40 hours at 20°C to an atmosphere having a relative humidity of 97.

The calcium carbonate filler used in the present invention is ground to obtain a suitable particle size distribution. The grinding process may be carried out  
30 either in a dry state in the absence of added hygroscopic or hydrophilic chemicals or in a wet state

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in an aqueous medium in which any dispersant employed is minimized and/or subsequently removed from the filler in a known manner. Wet ground material is subsequently dried to an extent such that the particulate material  
5 has an appropriate moisture content.

The calcium carbonate used in the invention may have been processed, e.g. by known purification, comminution and particle size classification procedures to have a suitable form prior to use to form the  
10 particulate product according to the present invention. However, following such processing the amount of hygroscopic or hydrophilic additives present is preferably minimized, as described earlier, e.g. by removing any such additives used by a washing process.

15 The calcium carbonate used in the present invention is treated with a hydrophobizing surface treatment agent and the treatment may be carried out prior to use by addition to thermoplastic polymeric material. Alternatively, the hydrophobizing agent, sometimes  
20 referred to as antagonizing agent, may be added directly to the thermoplastic polymer with which the calcium carbonate is to be compounded, before, during or after addition of the particulate product according to the present invention. For maximizing the effect of the  
25 hydrophobizing agent, complete surface treatment of the calcium carbonate is preferred prior to addition to the thermoplastic polymer.

Where the calcium carbonate filler used in the invention is surface treated, the  $d_{50}$  of the filler  
30 after treatment (which may differ slightly from the  $d_{50}$

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before such treatment) should be in the ranges defined above.

Use of surface treatment agents, which, when added to the inorganic particulate material which is dry, facilitate dispersion of the inorganic particulate material in hydrophobic polymeric material are well known. Suitable surface treatment agents are known to include aliphatic carboxylic acids having from 10 to 30 carbon atoms in their chain, including but not limited to, stearic acid, behenic acid, palmitic acid, arachidic acid, montanic acid, capric acid, lauric acid, myristic acid, isostearic acid and cerotic acid and mixtures thereof.

Further details concerning the surface treatment of calcium carbonate fillers for polymer compositions may be found in WO 99/61521, the contents of which are incorporated herein by reference for all purposes.

The production route employed for producing the calcium carbonate used in the present invention can be selected from the many procedures known to those skilled in the art. Further details regarding the production of suitable particulate calcium carbonate minerals for use in the invention may be found in WO 99/61521, the contents of which are incorporated herein by reference for all purposes.

The polymeric material to which the particulate calcium carbonate is added to form a composition may comprise, for example, a continuous thermoplastic polyolefin polymer matrix.

The particulate calcium carbonate may be incorporated in an application composition (to form an



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intermediate product which is then stretched to form the stretched end product) together with a thermoplastic polyolefin material and other optional conventional additives, e.g. a bonding or tackifying agent.

5       The process employed to form the intermediate product, and subsequently the stretched polyolefin film, from the thermoplastic material and the particulate calcium carbonate may be one or more of the methods well known in the art as described later.

10       In the intermediate film product and the subsequent stretched product, the thermoplastic polyolefin polymer may form from 20% to 80% by weight and the filler will form from 30% to 80% by weight of the composition, i.e. combination of the polymer plus filler. More  
15       preferably, the thermoplastic polymer forms from about 30% to about 55% by weight of the composition and the filler forms from about 45% to about 65% by weight of the composition.

20       The preferred thermoplastic polymer for us in the invention is a thermoplastic polyolefin, for example one which comprises more than about 50% by weight of olefin units and is referred to as polyolefin resin.

25       The polyolefin polymers (or resins) which can be used to provide the polyolefin resin, for example, include mono-olefin polymers of ethylene, propylene, butene or the like, or copolymers thereof as a main component. Typical examples of the polyolefin resin include polyethylene resins such as a low-density polyethylene, linear low-density polyethylene (ethylene-  
30        $\alpha$ -olefin copolymer), middle-density polyethylene and high-density polyethylene; polypropylene resins such as

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polypropylene and ethylene-polypropylene copolymer;  
poly(4-methylpentene); polybutene; ethylene-vinyl  
acetate copolymer; and mixtures thereof. These  
polyolefin resins may be obtained by polymerization in a  
5 known way, e.g. by the use of a Ziegler catalyst, or  
obtained by the use of a single site catalyst such as a  
metallocene catalyst. Above all, polyethylene resins  
are preferable, and linear low-density polyethylene  
(ethylene- $\alpha$ -olefin copolymer) and low-density  
10 polyethylene are most preferable. Furthermore, in view  
of the moldability, the stretchability and the like of  
the film, the melt index of the polyolefin resin is  
preferably in the range of about 0.5 to 5 g/10 min.

Other thermoplastic polymers which may be used in  
15 the practice of the present invention are thermoplastic  
elastomers, such as SBS.

Desirably, the filler includes at least 50% by  
weight, e.g. from 80% to 99% by weight of the calcium  
carbonate where one or more other fillers are employed  
20 together with the particulate product according to the  
present invention.

Examples of the other fillers include calcium  
carbonate (not in accordance with the invention), barium  
sulphate, calcium sulphate, barium carbonate, magnesium  
25 hydroxide, aluminum hydroxide, zinc oxide, calcium  
oxide, magnesium oxide, titanium oxide, silica and talc.  
The average particle diameter of the other filler is  
preferably 20  $\mu\text{m}$  or less, preferably 10  $\mu\text{m}$  or less,  
preferably in the range of 0.5 to 5  $\mu\text{m}$ . In order to  
30 improve the dispersibility of the other filler in the  
polyolefin resin, the other filler may be subjected to a

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surface treatment to render its surfaces hydrophobic, may be used. Examples of suitable surface treatment agents include the fatty acids such as stearic acid, specified earlier.

5       The composition ratio between the thermoplastic polymer and the calcium carbonate filler has an influence on the moldability and the stretchability of the film as well as the breathability and the moisture vapor transmission of the obtained film. If the amount  
10 of the filler is insufficient, adjacent micropores, which are required to be obtained by the interfacial separation of the polymer and the calcium carbonate filler from each other, are not continuous, so that a porous film having the good gas breathability and  
15 moisture vapor transmission cannot be obtained. On the contrary, if the amount of the calcium carbonate filler is excessive, defective molding occurs during the film forming process and the stretchability deteriorates, so that the sufficient stretching cannot be carried out.  
20 In view of these limiting factors, the composition ratio between the polymer and the calcium carbonate filler may be from 25 to 70 parts by weight of the polymer with respect to from 75 to 30 parts by weight of the calcium carbonate filler, e.g. from 30 to 60 parts by weight of  
25 the polymer with respect to 70 to 40 parts by weight of the calcium carbonate filler.

In the manufacture of a breathable film according to the present invention a concentrate or masterbatch of the thermoplastic polyolefin polymer resin and the  
30 calcium carbonate filler may first be produced by mixing and compounding prior to the film production stages.

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The mixture of ingredients to be blended by compounding may include in addition to the polymer and the filler other known optional ingredients conventionally employed in thermoplastic films, e.g. one  
5 or more of bonding agents, plasticisers, lubricants, anti-oxidants, ultraviolet absorbers, dyes, colorants. A bonding or tackifying agent, where employed, may facilitate bonding of the film after formation to another member, e.g. a non-woven fibrous layer, or one  
10 or more non-porous layers.

The thermoplastic polymer, the filler and, if necessary, other optional additives, may be mixed by the use of a suitable compounder/mixer e.g. a Henschel mixer, a super mixer, a tumbler type mixer or the like,  
15 and kneaded and may be pelletized, e.g. by the use of a single screw extruder or a twin-screw extruder which forms strands which may be cut or broken into pellet.

The masterbatch or concentrate, e.g. in the form of pellets, is melted and molded or shaped into the  
20 intermediate film (i.e. the film before stretching) by the use of a molding and film forming machine, as well known in the art. . Normally, the masterbatch, prior to the film forming step is "let down" to a suitable calcium carbonate content, using a polymer which may be  
25 the same as or different from the polymer of the masterbatch. For example, the masterbatch may be formed at a mineral filler content of the order of 70 wt.% which is let down to a mineral filler content of, for example, 55 wt.%

30 The intermediate may be a blown film, cast film or extruded film. Other types of films are also considered

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to be within the scope of the present invention provided the forming technique is compatible with filled films. Appropriate methods for producing the films according to the present invention will be readily apparent to the skilled artisan.

The intermediate film is then heated, e.g. to a temperature of about 5°C less than about the melting point of the thermoplastic polymer or more, and then stretched to at least about 1.2 times, preferably at least 2.5 times, its original length to thin the film and render it porous.

An additional feature of the thinning process is the change in opacity of the film. As formed, the film is relatively transparent but after stretching, it becomes opaque. In addition, while the film becomes orientated during the stretching process, it also becomes softer. Taking all these factors into consideration, and the desire to have a water vapor transmission rate of at least 100 grams per square meter per 24 hours, the film may, for example, be thinned to such an extent that it has a weight per unit area of less than about 35 grams per square meter for personal care absorbent article applications and a weight per unit area of less than about 18 grams per square meter for certain other applications.

The molding and film forming machine may for example comprise, as in the prior art, an extruder equipped with a T-die or the like or an inflation molding machine equipped with a circular die. The film production may be carried out at some time after the masterbatch production, possibly at a different

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manufacturing plant. In some cases, the masterbatch can directly be formed into the film without producing an intermediate product.

The film can be stretched in at least a uniaxial  
5 direction at a temperature of from room temperature to the softening point of the thermoplastic polymer in a known manner such as a roll method, an interdigitizing method, or a tenter method to bring about the  
10 interfacial separation of the polymer and the inorganic filler from each other, whereby a porous film can be prepared. The stretching may be carried out by one step or by several steps. Stretch magnification determines film breakage at high stretching as well as  
15 breathability and the moisture vapor transmission of the obtained film, and so excessively high stretch magnification and excessively low stretch magnification are desirably avoided. The stretch magnification is preferably in the range of 1.2 to 5 times, more preferably 1.2 to 4 times in at least a uniaxial  
20 direction. If biaxial stretching is carried out, it is possible that for example stretching in a first direction is applied in the machine direction or a direction perpendicular thereto, and stretching in a second direction is then applied at right angles to the  
25 first direction. Alternatively, the biaxial stretching may be carried out simultaneously in the machine direction and the direction perpendicular thereto. Any method known in the art or after developed can be applied in making the film in the method according to  
30 this aspect of the present invention.

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After the stretching, a heat setting treatment may be carried out if required in order to stabilize the shape of obtained voids. The heat setting treatment may be, for example, a heat setting treatment at a temperature in the range of from the softening point of the resin to a temperature less than about the melting point of the resin for a period of 0.1 to 100 seconds.

No particular restriction is put on the thickness of a breathable film produced of the present invention. The thickness should be such as to obtain film unlikely to tear or break and which has appropriate softness and good feel. Usually, the thickness of the breathable film is in the range of 5  $\mu\text{m}$  to 100  $\mu\text{m}$ , preferably 10  $\mu\text{m}$  to 70  $\mu\text{m}$ .

Generally, once the film is formed, it will have a weight per unit area of less than about 100 grams per square meter and after stretching and thinning its weight per unit area will be less than about 35 grams per square metre and more desirably less than about 18 grams per square metre.

The breathable film can be suitably utilized in applications requiring softness, for example, as the backing sheet of disposable diapers.

"Porous" as used in the present application includes but is not coextensive with "breathable" films.

A breathable film of the present invention having such properties may have a suitable breathability, moisture vapor transmission and feeling as well as excellent mechanical properties and long-term adhesive properties to be suitably used in products such as disposable diapers, body fluid absorbing pads and bed

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5 sheets; medical materials such as surgical gowns and  
base materials for hot compress; clothing materials such  
as jumpers, rainwear; building materials such as  
wallpapers and waterproof materials for roofs and house  
wraps; packaging materials for packaging desiccants,  
dehumidifying agents, deoxidizers, disposable body  
warmers; packaging materials for keeping the freshness  
of various articles and foods; separators for the cells;  
and the like. The breathable film is particularly  
10 desirable as a material used in products such as  
disposable diapers and body fluid absorbing pads. The  
breathable film may in such products be formed into a  
composite or laminate in one of the ways well known in  
the art with one or more other layers, e.g. a non-woven  
15 fibrous layer, e.g. by an adhesive or bonding agent.

Embodiments of the present invention will now be  
described, by way of example only, and with reference to  
the following Examples.

#### EXAMPLE 1

20 A chemical-free, ground calcium carbonate was used,  
produced by a low-solids sand-milling route. The  
calcium carbonate had a nominal  $d_{50}$  of  $0.6\mu\text{m}$ .

A 3 tonne (dry weight) sample of the carbonate was  
dewatered, dried and stearate coated by the addition of  
25 a stearate dose of 2.1 wt% (equivalent to 1 wt% per  
 $4.5\text{m}^2.\text{g}^{-1}$  of surface area). To ensure the product was  
free from oversize aggregates, the coated material was  
then passed through a Nisshin air-classifier to remove  
any material present with a  $d_{50}$  exceeding  $10\mu\text{m}$ .

30 Two tonnes of a coated final product were produced.  
The physical analyses of the uncoated and coated product



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are shown below in Tables 1 and 2 respectively. The physical analysis of the coated product was for three representative samples collected from the 2 tonne bulk sample.

5

Table 1

## Physical Analysis of Uncoated Product

Sedigraph Particle Size Analysis						Surface area (m <sup>2</sup> .g <sup>-1</sup> )	distribution steepness
+10um	-2um	-1um	-0.5um	0.25um	d <sub>50</sub>		
2.7	92.2	73.4	35.7	9.4	0.65	9.7	46

Table 2

## Physical Analysis of Coated Product (Carbonate A)

10

Mastersizer Particle Size Analysis						LOI (wt%) H <sub>2</sub> O pickup (wt%)
+10um	-2um	-1um	-0.5um	0.25um	d <sub>50</sub>	
1.2	82.6	62.8	34.6	8.7	0.72	2.1/0.19
Not measured						2.2/0.16
Not measured						2.6/0.14

The performance of a sample of the coated calcium carbonate material referred to above (hereafter Carbonate A) and a sample of a commercially available calcium carbonate having a d<sub>50</sub> of 1.27 (hereafter Carbonate B) were compared in a variety of LLDPE resins of differing densities at 65% filler (also containing 1500ppm of Irganox 1010 antioxidant).

The following masterbatch compositions were produced as shown in Table 3 which also indicates the single point viscosity (MI) and stiffness (density) of the resins employed (prior to the addition of any processing additive):

20

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Table 3

Compound	Carbonate	MI of PE	Density of PE
A	B	2.3	0.917
B	B	2.5	0.935
C	A	2.3	0.917
D	B	2.3	0.917
E	A	2.3	0.917
F	A	3.3	0.917
G	A	4.0	0.916
H	A	6.0	0.919
I	A	5.4	0.921
J	A	9.5	0.920

The LLDPE used in Compounds D and E contained 10% by weight of a polyethylene wax processing additive.

5        These compositions were compounded on a Werner and Pfleiderer ZSK40 compounder operating at an extruder speed of 300rpm and a throughput of 80kg.h<sup>-1</sup> with a die temperature of 220 °C

10       The compounds containing the polyethylene wax processing additive (Compounds D and E) were prepared on a Baker-Perkins MP2030 compounder operating at an extruder speed of 300rpm, a throughput of 5kg.h<sup>-1</sup> and a die temperature of 220°C.

15       The resulting masterbatch samples were then let down to nominal 50 or 55% calcium carbonate content and then extruded in a cast-film pilot line having 5 heating zones maintained at the following temperatures: 190°C, 200°C, 200°C, 210°C, 220°C and a die temperature of

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220°C, and subsequently stretched in machine direction. Extruder feed rates and speed of the stretching rollers were chosen to produce stretched films with a nominal thickness of 25µm.

- 5 The results obtained are set out in Table 4 below. The Moisture Vapour Transmission Rates (MVTR), measured in  $\text{g.H}_2\text{O.m}^{-2}.\text{day}^{-1}$ , of the films were measured as duplicate samples (using micropore membranes as controls) according to ASTM E - 96 (weight loss method)
- 10 at 37°C. The  $\text{CaCO}_3$  content of the film was measured by ashing at 450°C for 1 hour. The comments refer to the quality of the film produced in terms of its uniformity of thickness and ability to resist tearing.

Table 4

Film	Compound (filler content: stretch ratio)	$\text{CaCO}_3$ content	MVTR	Comments
1	control	49.9	2501	control film
2	A (50: x4)	50.6	2174	Pass
3	A (50: x3)			Fail
4	C (50: x4)	52.1	1999	Pass
5	C (50: x3)			Fail
6	B (50: x4)			Fail
7	B (50: x5)			Fail
8	J (50: x4)	48.5	496	Fail
9	J (50: x3)			Fail
10	H (50: x4)			Fail
11	H (50: x5)	50.5	2918	Fail
12	F (50: x4)	50.5	1705	Fail
13	F (50: x5)	48.8	2169	Pass
14	I (50: x4)	49.8	654	Fail
15	I (50: x5)	48.1	2052	Pass
16	G (50: x4)	52.2	2049	Fail
17	G (50: x5)	51.3	3195	Pass
18	E (50: x4)	45.8	40	Fail
19	E (50: x5)	44.6	21	Fail
20	G (55: x4)	54.5	3029	Fail

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Film	Compound (filler content: stretch ratio)	CaCO <sub>3</sub> content	MVTR	Comments
21	G (55: x5)	55.3	3478	Pass
22	C (55: x4)	54.0	2438	Fail
23	C (55: x5)	54.2	3277	Pass
24	A (55: x4)	56.4	3673	Pass
25	A (55: x5)	54.6	3147	-
26	B (55: x4)			Fail
27	B (55: x5)	55.0	3679	Fail
28	J (55: x4)			Fail
29	J (55: x5)			-
30	H (55: x4)			Fail
31	H (55: x5)	54.2	4137	Fail
32	F (55: x4)	51.9	1853	Fail
33	F (55: x5)	51.7	2981	Pass
34	I (55: x4)			Fail
35	I (55: x5)	52.3	2339	Fail
36	E (55: x4)			Fail
37	E (55: x5)	57.7	1329	Fail

A number of the films obtained were not uniform, principally as a result of limitations in the stretching equipment employed, and are thus marked "failed".

- 5 Although some of these films were sampled for MVTR, the results obtained for these films are of limited comparative value.

#### Example 2

- 10 A chemical-free, ground calcium carbonate was used, produced by low-solids sand-milling route. The slurry was hydrocycloned to eliminate coarse material, dewatered, dried and stearate treated by the addition of a stearate dose of 1.25wt % (equivalent to 1 wt% per  $4.5\text{m}^2\text{g}^{-1}$  of surface area). The product had a  $d_{50}$  of 0.81  $\mu\text{m}$  as measured by Sedigraph (subsequently referred to as Carbonate C).
- 15

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The performance of Carbonate C in an LLDPE resin at various filler level contents was compared to that of a commercially available calcium carbonate having a  $d_{50}$  of 1.27 (hereafter Carbonate D).

5        60 weight % (of filler) masterbatches of carbonates C and D were prepared on a Werner and Pfleiderer ZSK40 twin screw extruder. The equipment was operated at a feed rate of 100 kg masterbatch  $\text{hr}^{-1}$  with barrel temperatures of 170°C, 190°C, 200°C, 210°C, and a die  
10       temperature of 220°C, and a drive torque of 50%. Masterbatches also contained 1500 ppm of Irganox 1010.

The resulting masterbatches were let down with virgin LLDPE to attain required nominal levels of 45, 50 or 55 weight % filler and extruded in a cast-film pilot  
15       line with 5 heating barrels maintained at temperatures of 190°C, 200°C, 200°C, 210°C, 220°C, respectively, and a die maintained at a temperature of 220°C. The extruded film was subsequently stretched in the machine  
20       direction. Extruder rates and the speed of stretching rollers were chosen to produce microporous films with a nominal thickness of 25 $\mu\text{m}$ .

The Moisture Vapour Transmission Rates (MVTR), in  $\text{g.H}_2\text{O.m}^{-2}.\text{day}^{-1}$ , of the films were measured as duplicate samples (using micropore membranes as controls)  
25       according to ASTM E-96 (weight loss method) at 37°C. Results are shown in Table 5. The actual percentage of filler in the films was measured by loss on ignition at 400 °C. It is therefore possible to normalise all MVTR values to nominal filler loading levels of 45, 50, and  
30       55 weight %. These values are shown in Table 5.

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Table 5

Film Description	% Filler	MVTR	MVTR corrected
Carbonate C, 45 wt.%, x4 stretch	43.7	925	--
Carbonate C, 45 wt.%, x5 stretch	43.7	799	1209
Carbonate C, 45 wt.%, x6 stretch	43.7	460	--
Carbonate C, 50 wt.%, x4 stretch	50.4	2378	--
Carbonate C, 50 wt.%, x5 stretch	50.4	2598	2516
Carbonate C, 50 wt.%, x6 stretch	50.4	2365	--
Carbonate C, 55 wt.%, x4 stretch	55.5	3302	--
Carbonate C, 55 wt.%, x5 stretch	55.5	3464	3402
Carbonate C, 55 wt.%, x6 stretch	55.5	3778	--
Carbonate D, 45 wt.%, x4 stretch	44.3	741	--
Carbonate D, 45 wt.%, x5 stretch	44.3	792	975
Carbonate D, 45 wt.%, x6 stretch	44.3	1181	--
Carbonate D, 50 wt.%, x4 stretch	47.9	1501	--
Carbonate D, 50 wt.%, x5 stretch	47.9	1710	2264
Carbonate D, 50 wt.%, x6 stretch	47.9	1510	--
Carbonate D, 55 wt.%, x4 stretch	53.9	3068	--
Carbonate D, 55 wt.%, x5 stretch	53.9	3295	3610
Carbonate D, 55 wt.%, x6 stretch	53.9	3534	--

Reference to Table 5 shows that for most stretching ratios and filler loadings Carbonate C gives rise to higher breathability than Carbonate D.

CLAIMS

1. The use of a ground particulate calcium carbonate material having a  $d_{50}$  of less than  $1.0\text{ }\mu\text{m}$  as a mineral filler in a stretched thermoplastic polyolefin  
5 film, for the purpose of increasing the moisture vapour permeability of said film.
2. The use as claimed in claim 1, wherein the particulate calcium carbonate material has a  $d_{50}$  greater than  $0.3\text{ }\mu\text{m}$ .
- 10 3. The use as claimed in claim 2, wherein the particulate calcium carbonate material has a  $d_{50}$  greater than  $0.5\text{ }\mu\text{m}$ .
4. The use as claimed in claim 1, 2 or 3, wherein the particulate calcium carbonate material has a  $d_{50}$  less  
15 than  $0.8\text{ }\mu\text{m}$ .
5. The use as claimed in any preceding claim, wherein the calcium carbonate has been surface treated with a hydrophobizing agent.
6. The use as claimed in claim 5, wherein the  
20 hydrophobizing agent is an aliphatic carboxylic acid having from 10 to 30 carbon atoms.
7. The use as claimed in claim 6, wherein the hydrophobizing agent is stearic acid.
8. The use as claimed in any preceding claim,  
25 wherein the polyolefin is polyethylene.
9. The use as claimed in claim 8, wherein the polyethylene is linear low-density polyethylene or low-density polyethylene.
10. A method of increasing the moisture vapour  
30 permeability of a stretched, mineral-filled thermoplastic polyolefin film which method comprises

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using, as the mineral filler, a ground calcium carbonate having a  $d_{50}$  of less than 1.0  $\mu\text{m}$ .

11. A method according to claim 10, wherein the particulate calcium carbonate material has a  $d_{50}$  greater  
5 than 0.3  $\mu\text{m}$ .

12. A method as claimed in claim 11, wherein the particulate calcium carbonate material has a  $d_{50}$  greater than 0.5  $\mu\text{m}$ .

13. A method as claimed in claim 10, 11 or 12,  
10 wherein the particulate calcium carbonate material has a  $d_{50}$  less than 0.8  $\mu\text{m}$ .

14. A method as claimed in any one of claims 10 to 13, wherein the calcium carbonate has been surface treated with a hydrophobizing agent.

15 15. A method as claimed in claim 14, wherein the hydrophobizing agent is an aliphatic carboxylic acid having from 10 to 30 carbon atoms.

16. A method as claimed in claim 15, wherein the hydrophobizing agent is stearic acid.

20 17. A method as claimed in any one of claims 10 to 16, wherein the polyolefin is polyethylene.

18. A method as claimed in claim 17, wherein the polyethylene is linear low-density polyethylene or low-density polyethylene.



# INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08J5/18 C08K3/26 C08L23/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 227 037 A (MITSUI TOATSU CHEMICALS) 1 July 1987 (1987-07-01) column 5; examples 1-9 column 7 -column 8; table 1 claims 1-5	1-18
X	EP 0 352 802 A (HERCULES INC) 31 January 1990 (1990-01-31) claims 1-25	1-18
X	EP 0 854 164 A (LEER KONINKLIJKE EMBALLAGE) 22 July 1998 (1998-07-22) claims 1-4	1-18

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Information on patent family members

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